

PATENT SPECIFICATION

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- (21) Application No. 50947/74 (22) Filed 25 Nov. 1974
 (61) Patent of Addition to No. 1,451 280 dated 4 June 1974
 (31) Convention Application No. 422 123 (32) Filed 5 Dec. 1973 in
 (33) United States of America (US)
 (44) Complete Specification published 28 Sept. 1974
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(54) ORGANIC REINFORCING FILLERS FOR SILICONE RUBBER

(71) We, MOBIL OIL CORPORATION, a corporation organised and existing under the laws of the State of New York, United States of America, of 150 East 42nd Street, New York, New York 10017, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with organic reinforcing fillers for silicone rubbers and their preparation.

Various materials have been proposed and used as reinforcing fillers for silicone rubber. Treated fine particle silicas are the major reinforcing fillers presently in use.

In our co-pending Application No. 24744/74 (Serial No. 1,451,280), we have described and claimed a process for producing an organic reinforcing filler for rubber, which comprises polymerizing a reaction mixture comprising styrene, divinylbenzene, and an anionic polymerization initiator dispersed in a liquid aliphatic hydrocarbon slurring medium in the presence of from 0.1 to 10 weight percent

mixture of (1) and (2), whereby when the process is carried out with an initiator defined in (1) the slurry polymerization is terminated with a terminating agent selected from oxygen followed by acetic acid, air, carbonyl sulphide, propylene sulphide, N-oxydiethylene - benzothiazole - 2 - sulphenamide, benzothiazyl disulphide, or dipentamethylene thiuram hexasulphide and, when the process is carried out with an initiator as defined in (2) or (3), the slurry polymerization is optionally terminated with one of the above terminating agents.

We have now found that when the anionic polymerisation of styrene with a divinylbenzene cross-linking agent is terminated with certain other terminating agents, a finely divided, solid, cross-linked polymer containing functional groups which are reactive with silicone rubber during curing thereof, is obtained which is useful as a reinforcing filler for silicone rubber.

According to one aspect of the present invention, therefore, we provide a process for producing an organic reinforcing filler for silicone rubber, which comprises polymerizing a reaction mixture comprising

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...the anionic polymerization initiator comprising an alkali metal-bearing compound 90

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mixture of (1) and (2), whereby when the process is carried out with an initiator defined in (1) the slurry polymerization is terminated with a terminating agent selected from oxygen followed by acetic acid, air, carbonyl sulphide, propylene sulphide, N-oxydiethylene - benzothiazole - 2 - sulphenamide, benzothiazyl disulphide, or dipentamethylene thiuram hexasulphide and, when the process is carried out with an initiator as defined in (2) or (3), the slurry polymerization is optionally terminated with one of the above terminating agents.

We have now found that when the anionic polymerisation of styrene with a divinylbenzene cross-linking agent is terminated with certain other terminating agents, a finely divided, solid, cross-linked polymer containing functional groups which are reactive with silicone rubber during curing thereof, is obtained which is useful as a reinforcing filler for silicone rubber.

According to one aspect of the present invention, therefore, we provide a process for producing an organic reinforcing filler for silicone rubber, which comprises polymerizing a reaction mixture comprising styrene, divinylbenzene, in an amount of from 0.5 to 15 weight percent based on the styrene, and an anionic polymerization initiator dispersed in a liquid aliphatic hydrocarbon slurring medium in the presence of from 0.1 to 10 weight percent, based upon the styrene reactant, of an AB or ABA block copolymer dispersant, in which segment A is derived from styrene and is an amount of from 5 to 80 weight percent of the total block copolymer, and segment B is derived from t-butylstyrene, butadiene, isoprene, or 2,2-dimethylbutadiene, to produce a finely divided, solid, cross-linked copolymer containing functional groups which are reactive with silicone rubber during curing thereof, the anionic polymerization initiator comprising an alkali metal-bearing compound

which is capable of initiating the polymerization of styrene but which does not impart to the resulting copolymer groups which are reactive with silicone rubber during curing thereof, and the polymerization being terminated with a terminating agent selected from hexamethylcyclotrisiloxane, vinyltrimethylchlorosilane, allyldimethylchlorosilane, vinylmethyldichlorosilane, allylmethyldichlorosilane, air followed by acetyl chloride to form a peracetate ester, and air followed by benzoyl chloride to form a perbenzoate ester.

The block copolymer dispersant controls the particles of the resulting cross-linked polymer to a fine size, desirably less than 2000Å. The groups produced provide effective bonding of the polymer filler particles to the silicone rubber and in so doing, provide the desired reinforcement.

The anionic initiator preferably comprises an alkali metal derivative of a monomeric hydrocarbon compound and more preferably comprises an alkali metal alkyl, such as ethyl-lithium, butyl-lithium, sec-butyl-lithium or amyl-lithium as well as the corresponding sodium compounds, or lithium or sodium salts of materials such as alpha-methyl styrene, 1,1-diphenylethylene or naphthalene. Such materials produce a cross-linked "living" polymer in the slurry polymerization.

The amount of anionic catalyst or initiator that is used is generally in the range of 10^{-1} or 10^{-4} moles per 100 grams of styrene reactant.

The aliphatic hydrocarbon slurring medium can be normal or branched chain, paraffinic or monoolefinic and can contain at least three, and more desirably, four to seven, carbon atoms. Typical slurring media include butane, pentane, isopentane, hexane, 2,2-dimethylbutane, butene, pentene, as well as mixtures such as petroleum ether, pentane-pentene and hexane-hexene.

The polymerization process of the invention is preferably carried out at a temperature of from 20°C. and 120°C. The desired polymerization temperature is determined in part by the reflux temperature of the slurring medium. It is, however, possible to use pressure in order to elevate the reflux temperature of the slurring medium.

The divinylbenzene (o-, p-, or mixed isomers) serves as a cross-linking agent.

The styrene content of the block copolymer dispersing agent which is used in the polymerisation is preferably 5 to 50 weight percent of the total block polymer. Particularly preferred are block copolymers of styrene and *t*-butyl styrene.

The materials which are used as terminating agents are compounds that react with the styryl anion on the filler particles to form the functional groups attached to

the polymer particles which, in turn, react with a silicone rubber molecule during a conventional cure.

As described in our co-pending application mentioned above, the existence of functional groups which react with a rubber can in principal be determined by measuring the 300 percent modules of the cured material (rubber plus filler). The use of reactive fillers produces a higher modules than non-reactive fillers.

The organic reinforcing fillers of this invention are highly effective when blended with a silicone rubber base stock and the usual rubber curing components and then cured. The terminal reactive groups help to promote the rubber cure and bond to the silicone rubber molecule during the cure reaction.

The curable silicone rubbers which may be used with the reinforcing fillers of the present invention include, for example, dimethyl siloxane gum rubber and its copolymers with phenyl methyl siloxane; methyl phenyl siloxanes; methyl vinyl-siloxanes; methyl hydrogen siloxanes; and diphenyl siloxanes. The amount of reinforcing filler used will generally be from 10 to 100 parts (by weight) per 100 parts (by weight) of silicone rubber, i.e., PHR.

A discussion of compounding and vulcanizing silicone rubbers can be found on pages 388-398 of "Introduction to Rubber Technology" edited by Maurice Morton, Reinhold Publishing Corporation, New York (1959).

The following example, which is given by way of illustration only, is given to assist in the understanding of the invention. Examples 1 to 8 of co-pending application No. 24744/74 (Serial No. 1,451,280) illustrate the preparation of suitable block polymer dispersants.

EXAMPLE

A crosslinked styrene-divinylbenzene polymer of fine particle size was prepared by polymerization of 30 g. styrene and 3 g. 55% divinylbenzene in 500 ml. hexane using 2.89 ml. of 2N S-butyllithium as catalyst and 1.5 g. of styrene-*t*-butylstyrene block copolymer of Example 4 of co-pending application No. 24744/74 (Serial No. 1,451,280) as a dispersant (20,000 - 80,000 M.W. blocks respectively) under nitrogen. At the end of 1 hour reaction at reflux the solution was treated with 3.0 ml. of dry, air free *t*-butylstyrene for 30 minutes followed by 2.0 g. of hexamethylcyclotrisiloxane in 5.0 ml. of tetrahydrofuran for 2.5 hours. This was followed by the addition of 1.26 ml. of allyldimethylchlorosilane. The resulting product was blended with 118 g. of dimethyl siloxane rubber (General Electric Co. No. SE-76) dissolved in hexane and the

5 mixture precipitated into methanol to give a product containing 28 parts of filler particles per 100 parts of silicone rubber. This product was mixed with 2 parts of dicumylperoxide per 100 parts of silicone rubber and cured in a press at 135°C. for 35 minutes. The cured rubber had the following properties:

10 Tensile:

Elongation to Break — 696%
Break Strength — 1680 kg.m⁻²
(344 psi)

15

Shore A hardness — 48

Modulus at 300% elongation —
74 kg.m⁻² (152 psi)

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WHAT WE CLAIM IS:—

1. A process for producing an organic reinforcing filler for silicone rubber, which comprises polymerizing a reaction mixture comprising styrene, divinylbenzene, in an amount of from 0.5 to 15 weight percent based on the styrene, and an anionic polymerization initiator dispersed in a liquid aliphatic hydrocarbon slurring medium in the presence of from 0.1 to 10 weight percent, based upon the styrene reactant, of an AB or ABA block copolymer dispersant, in which segment A is derived from styrene and is in an amount of from 5 to 80 weight percent of the total block copolymer, and segment B is derived from *t*-butylstyrene, butadiene, isoprene, or 2,2-dimethylbutadiene, to produce a finely divided, solid, cross-linked copolymer containing functional

groups which are reactive with silicone rubber during curing thereof, the anionic polymerization initiator comprising an alkali metal-bearing compound which is capable of initiating the polymerization of styrene but which does not impart to the resulting copolymer, groups which are reactive with silicone rubber during curing thereof, and the polymerization being terminated with a terminating agent selected from hexamethylcyclotrisiloxane, vinyltrimethylchlorosilane, allyldimethylchlorosilane, vinylmethyldichlorosilane, allylmethyldichlorosilane, air followed by acetyl chloride to form a peracetate ester, and air followed by benzoyl chloride to form a perbenzoate ester.

2. A process according to claim 1, in which the initiator comprises an alkali metal derivative of a monomeric hydrocarbon compound.

3. A process according to claim 2, in which the initiator comprises butyl-lithium.

4. A process for producing an organic reinforcing filler for rubber substantially as herein described in the Example.

5. An organic reinforcing filler for silicone rubber produced by a process as claimed in any of claims 1 to 4.

6. A curable silicone rubber composition comprising a silicone rubber and a reinforcing filler as claimed in claim 5.

7. A cured silicone rubber composition formed by curing a composition as claimed in claim 6.

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